



# Conversion of cellulose to hydrocarbon fuels by progressive removal of oxygen

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## ABSTRACT

We report a catalytic process to convert cellulose into liquid hydrocarbon fuels (diesel and gasoline), using a cascade strategy to achieve the progressive removal of oxygen from biomass, allowing the control of reactivity and facilitating the separation of products. The process starts with the deconstruction of solid cellulose in an aqueous solution of sulfuric acid yielding an equi-molar mixture of levulinic acid and formic acid. The formic acid in this mixture can then be used (upon decomposition to  $H_2$  and  $CO_2$ ) to reduce levulinic acid to  $\gamma$ -valerolactone (GVL) in the sulfuric acid solution over a Ru/C catalyst. The formation of GVL allows strategies for the separation and recycling of the sulfuric acid used in the cellulose deconstruction step. This GVL product, with residual amounts of sulfur, can be upgraded to 5-nonanone with high yields (90%) in a single reactor by using a dual catalyst bed of Pd/Nb<sub>2</sub>O<sub>5</sub> plus ceria-zirconia. The 5-nonanone product is hydrophobic and separates spontaneously from water, yet possesses a functional group that can be used to control the structure and molecular weight of hydrocarbon fuel components formed in downstream catalytic upgrading treatments.

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## 1. Introduction

Currently, the transportation sector of our society consumes approximately one third of the total energy produced in the world, and this transportation energy is derived almost exclusively from oil [1]. However, the utilization of petroleum involves various issues (accumulation of  $CO_2$ , diminishing reserves, economic and political problems) that are stimulating the search for alternative renewable resources, such as biomass, for the generation of transportation fuels [2,3]. The production of ethanol by means of an anaerobic fermentation of corn and sugar cane-derived sugars is, at the present time, the primary technology for the generation of liquid fuels from biomass and accounts for 90% of the total biofuel usage [4]. However, the low energy-density of ethanol compared with conventional hydrocarbon fuels (leading to lower gas mileage), its high solubility in water (that causes water from the atmosphere to absorb in the gasoline/ethanol mixture) and the use of edible biomass as a carbon feedstock (creating a competition with food production for land use) limit its use as a transportation fuel. These limitations can be overcome by converting non-edible lignocellulosic biomass into liquid hydrocarbon fuels chemically similar to those currently used in the transportation sector so that they are compatible with existing fuel distribution infrastructure [5]. In this respect, the gasification of biomass to synthesis gas ( $H_2/CO$ ) coupled with Fischer-Tropsch processes, commonly

known as *biomass to liquid* (BTL) [6]; the pyrolysis of biomass integrated with hydrodeoxygenation [7] or upgrading over zeolites [8]; and the aqueous-phase processing of carbohydrates to hydrocarbon fuels [9,10] are potential alternatives to the bioethanol industry.

Recently, our group has developed a process for the catalytic upgrading of levulinic acid to 5-nonanone, with the intermediate formation of  $\gamma$ -valerolactone (GVL) [11]. Since levulinic acid is an important biomass derivative that is obtained by acid hydrolysis of lignocellulosic wastes [12], this route can potentially serve to produce liquid transportation fuels from biomass. In the present paper, we have extended this route from solid biomass (cellulose) to liquid hydrocarbon fuels (diesel and gasoline) by developing a cascade approach (Fig. 1). This strategy is useful to achieve progressive deoxygenation of the biomass derivatives allowing better control of reactivity and facilitating the separation/recycling of products. In this process, outlined in Fig. 1, we first employ an aqueous solution of sulfuric acid to deconstruct solid cellulose by hydrolysis producing glucose, which is subsequently dehydrated under acid conditions to generate an equi-molar mixture of levulinic acid and formic acid. Formic acid in this aqueous acid solution is decomposed to  $H_2$  and  $CO_2$ , and this  $H_2$  is used to reduce the levulinic acid to GVL over a Ru/C catalyst. The GVL product is more hydrophobic than levulinic acid, thereby enabling selective separation of sulfuric acid from GVL, and allowing most of the acid to be recycled back to the cellulose deconstruction reactor. An aqueous solution of GVL containing smaller amounts of sulfuric acid is then passed over a sulfur-tolerant niobia-supported palladium catalyst in the presence of  $H_2$  to produce pentanoic acid, followed by conver-

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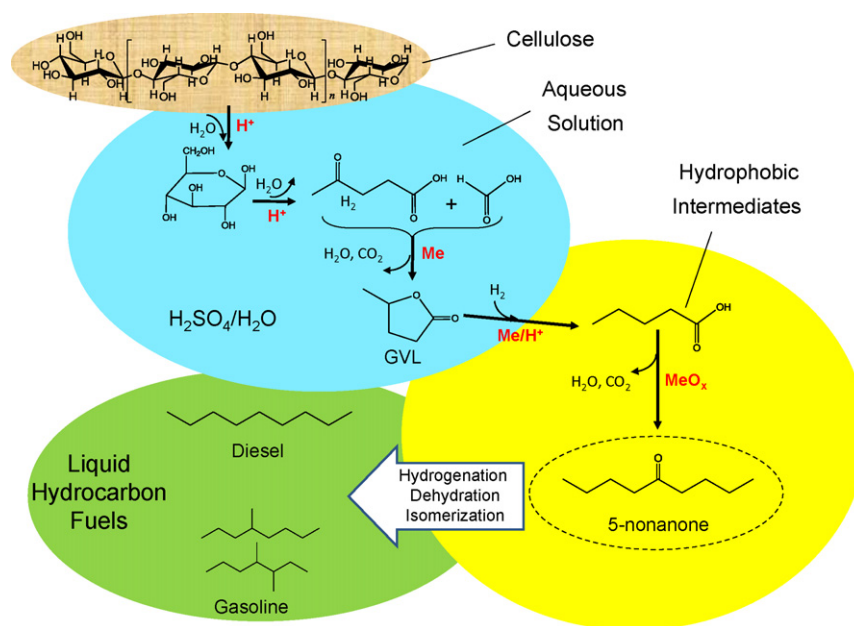


Fig. 1. Strategy for the conversion of solid cellulose to liquid hydrocarbon fuels.  $H^+$ : acid sites; Me: metal sites;  $MeO_x$ : metal oxide sites.

sion to 5-nonanone by ketonization [13] with high yields over a ceria-zirconia catalyst. This ketonization reaction achieves simultaneous C–C coupling and deoxygenation of pentanoic acid (through formation of  $CO_2$  and  $H_2O$ ). The hydrophobic organic stream of 5-nonanone (that separates spontaneously from water) can be further processed to liquid hydrocarbon fuels with controlled structure for diesel or gasoline applications by means of well-established hydrogenation, dehydration and/or isomerization reactions.

## 2. Experimental

### 2.1. Catalysts preparation

$Pd(5\%)/Nb_2O_5$  was prepared by incipient wetness impregnation (defined as the condition where the impregnation liquid containing the metal salt is added to fill the pore volume of the catalyst support, equal to 0.6 mL per gram of  $Nb_2O_5$ ) of a commercial niobium oxide (HY-340 from CBMM-Brazil, B.E.T. area =  $118\text{ m}^2\text{ g}^{-1}$ ) with an aqueous solution of  $Pd(NO_3)_2 \cdot xH_2O$  (Aldrich, 99%). The catalyst was dried at 380 K overnight, followed by calcination at 538 K in flowing air ( $250\text{ cm}^3(\text{STP})\text{ min}^{-1}$ ,  $1\text{ K min}^{-1}$  ramp) for 2 h. The ceria-zirconia catalyst with Ce:Zr molar ratio of 1:1 was prepared according to Serrano-Ruiz et al. [14]. A commercial  $Ru(5\%)/C$  catalyst (Sigma–Aldrich) was reduced at 673 K ( $2\text{ K min}^{-1}$  ramp, 4 h hold) while flowing  $H_2$  ( $100\text{ cm}^3(\text{STP})\text{ min}^{-1}$ ) and then passivated with 2%  $O_2$  in He ( $100\text{ cm}^3(\text{STP})\text{ min}^{-1}$ ) at ambient temperature for 4 h, prior to use in the conversion of levulinic acid to GVL in a batch reactor. The USY-zeolite catalyst (Engelhard/BASF) used for 5-nonanol dehydration/isomerization was calcined *in situ* under flowing air ( $25\text{ cm}^3(\text{STP})\text{ min}^{-1}$ ) at 773 K ( $8\text{ K min}^{-1}$  ramp) for 2 h prior to collecting reaction kinetics data.

### 2.2. Cellulose deconstruction to levulinic acid and formic acid

Microcrystalline cellulose (8 g, 5% moisture, Sigma–Aldrich) with an average size of  $20\text{ }\mu\text{m}$  and a 0.5 M sulfuric acid solution (92 g) were loaded into a 450 mL Parr Instruments alloy C-276 batch reactor equipped with a variable speed mechanical stir and Teflon liner. The reactor was pressurized with inert gas (35 bar) and heated to 423 K ( $1.4\text{ K min}^{-1}$  ramp) with a 590 W electric heating

mantle. The reactor was maintained at 423 K for 6 h while stirring at 600 rpm. At the end of the reaction time the heating mantle was removed and the reactor was cooled with compressed air. A liquid sample (400  $\mu\text{L}$ ) was collected, syringe filtered (0.2  $\mu\text{m}$  membrane), and analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector). After a cycle of cellulose deconstruction, another batch of microcrystalline cellulose (8 g, 5% moisture) was added to the reaction mixture and the vessel was resealed. The same procedure as above was performed for five cycles. The solid remaining at the end of the reaction was separated from the solution via vacuum filtration and an elemental analysis for C, H, and S was performed (Galbraith Labs., Knoxville, TN). The elemental analysis results indicated that the remaining solid composition was 67.32 wt% carbon and 4.83 wt% hydrogen, with no significant amount of sulfur adsorbed on these solids (0.06 wt%). Analysis by HPLC of the liquid obtained after five deconstruction steps showed that the number of moles of formic acid produced was equal to number of moles of levulinic acid formed (within 5%). Experiments performed without initially pressurizing the batch reactor (prior to heating) showed similar levulinic acid and formic acid yields (57% yield).

### 2.3. Levulinic acid reduction to GVL

The solution of levulinic acid and formic acid resulting from the 5-cycle cellulose deconstruction experiment described above was reacted over a 5 wt%  $Ru/C$  catalyst (Sigma–Aldrich). The catalyst (1.02 g) and a sample of the solution prepared from the 5-cycle cellulose deconstruction experiment above (40 g, 15.2 wt% levulinic acid, 6.6 wt% formic acid, 0.5 M  $H_2SO_4$ ) were loaded into a 450 mL Parr Instruments alloy C-276 batch reactor equipped with a variable speed mechanical stir and Teflon liner. The reactor was purged with inert gas, pressurized with hydrogen (35 bar) at ambient temperature, and stirred at 600 rpm. The reactor was heated to 423 K ( $1.4\text{ K min}^{-1}$  ramp) and then held constant for 4 h. Samples (500  $\mu\text{L}$ ) were collected during reaction and analyzed by HPLC. The rates of conversion of formic acid and levulinic acid are similar for the reaction conditions tested. Essentially a quantitative yield of GVL was observed at approximately 2 h reaction time at 423 K. Degradation of GVL was observed at reaction times longer than the time required

to completely convert levulinic acid to GVL (e.g., 10% degradation in 10 h). The pH of the solution remained constant during levulinic acid reduction.

#### 2.4. GVL extraction with ethyl acetate

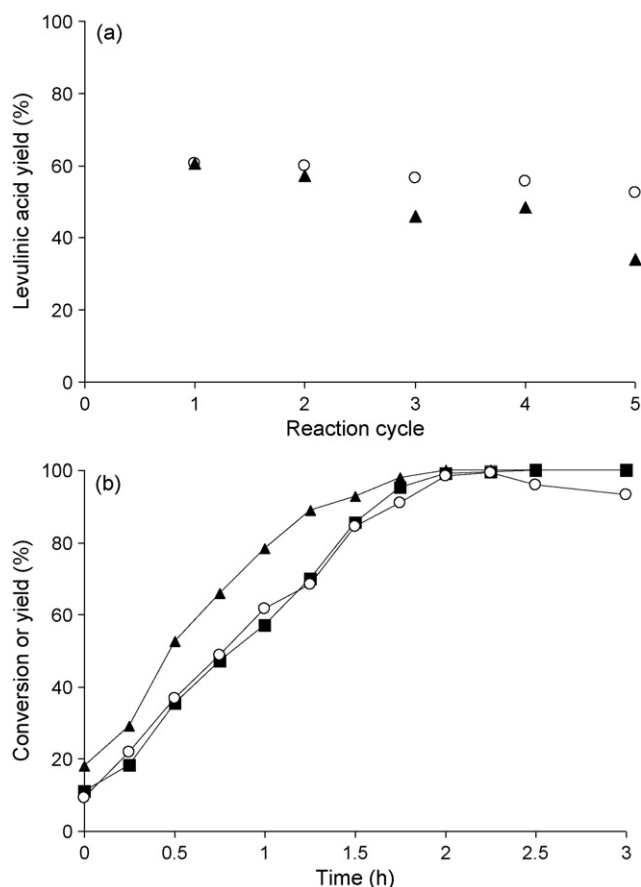
Ethyl acetate (96%, Sigma–Aldrich) was used to extract GVL from the sulfuric solution prepared by the reduction of levulinic acid. A sample (5.00 g, 1.07 g mL<sup>-1</sup>) of the acidic GVL solution was mixed with ethyl acetate (5.00 g) in a sealed glass container and shaken vigorously for 1 min. The solution was allowed to settle and the ethyl acetate layer was removed with a transfer pipette (5.31 g). The remaining aqueous layer (4.74 g, 1.06 g mL<sup>-1</sup>) was analyzed by HPLC. It was determined that 76% of the GVL was extracted into the ethyl acetate as well as 3% of the H<sub>2</sub>SO<sub>4</sub> and 6% of the water. Extraction experiments were performed for solutions of varying concentrations of GVL (5, 20, 35, 50 wt%) and sulfuric acid (0.2, 0.5, 1.0 M). Equal masses of aqueous solution and ethyl acetate were used for the extraction following the same procedure described above. The percent extraction for compound *i* is calculated as the moles of *i* transferred to the ethyl acetate layer divided by the moles of *i* initially in the aqueous layer prior to ethyl acetate addition.

#### 2.5. Conversion of GVL to pentanoic acid and 5-nonanone

The reaction kinetics studies were carried out in an upflow reaction system described in detail elsewhere [15]. The catalyst (3.5 g of Pd(5%)/Nb<sub>2</sub>O<sub>5</sub>) was fixed in a 1/4 in. Hastelloy C-276 tubular reactor between two end-plugs of carbon wool. For the dual catalyst bed experiments, the tubular reactor was loaded first with Pd(5%)/Nb<sub>2</sub>O<sub>5</sub> (3.0 g), followed by ceria–zirconia (5.0 g). Both beds were separated by a carbon wool plug. The reactor was surrounded by aluminum blocks heated externally by a well-insulated furnace (Applied Test Systems Inc.). A K-type thermocouple (Omega) was attached to the outside of the reactor to measure temperature, which was controlled with a 1600 series type temperature controller (Dwyer Instruments). Prior to reaction kinetics studies, fresh catalyst was reduced in flowing H<sub>2</sub> (100 cm<sup>3</sup>(STP) min<sup>-1</sup>) at 538 K (1 K min<sup>-1</sup> ramp) for 3 h, and then heated to the reaction temperature under flowing H<sub>2</sub>. The flow-rate of H<sub>2</sub> was fixed with a Brooks Model 5850 mass-flow controller. The system pressure was controlled by a backpressure regulator (GO Regulator, Model BP-60). A liquid solution containing various amounts (30–40 wt%) of GVL (Sigma–Aldrich) and sulfuric acid (0.02–0.04 M) in deionized water was introduced into the reactor using an HPLC pump (Lab Alliance Series 1) along with a H<sub>2</sub> co-feed flow of 30 cm<sup>3</sup>(STP) min<sup>-1</sup>. The effluent liquids (organic and aqueous) were collected at room temperature in a gas–liquid separator, drained periodically and analyzed by GC–MS (Shimadzu GC-2010 with a mass spectrometer and DB-5ms column from Alltech) and GC (Shimadzu GC-2010 with a FID detector and Rtx-5 column from Alltech). The effluent gas stream was analyzed on-line by gas chromatography using two different gas chromatograms operating in parallel. A Shimadzu GC-8A (equipped with TCD detector and an Alltech packed column model HayeSep DB 100/120) was used to detect CO, CO<sub>2</sub> and H<sub>2</sub>S. A Varian GC (Saturn 3) using a FID detector and a GS-Q capillary column (J&W Scientific) was used to detect other volatile organic compounds. The overall carbon balance gave recoveries ranging from 93% to 111%, and the sulfur balances ranged from 73% to 111%.

#### 2.6. Dehydration/isomerization of 5-nonanol to branched alkenes

The dehydration and isomerization of 5-nonanol was carried out over a USY–zeolite catalyst (Engelhard/BASF). The catalyst was loaded into a 1/4 in. tubular stainless steel reactor operating in an upflow configuration. Prior to reaction, the catalyst was cal-



**Fig. 2.** Results for cellulose deconstruction and levulinic acid reduction to GVL. (a) Levulinic acid yield per cycle (▲) and cumulative yield (○) for the deconstruction of cellulose in 0.5 M sulfuric acid at 423 K; (b) Conversions and yield for the batch processing of the cellulose-derived levulinic acid (—■—) and formic acid (---▲---) solution, in sulfuric acid, to GVL (—○—) over Ru/C at 423 K.

cined under flowing air (25 cm<sup>3</sup>(STP) min<sup>-1</sup>) at 773 K (8 K min<sup>-1</sup> ramp) for 2 h. The reactor was cooled to the reaction temperature (573 and 623 K) and pure 5-nonanol (Sigma–Aldrich) was introduced.

### 3. Results

As described in Section 2, the deconstruction step of our cascade approach was carried out using dilute aqueous solutions of sulfuric acid (0.5 M) at 423 K by adding solid cellulose to the reactor in progressive stages. Using this approach, we avoid having high levels of cellulose in the slurry at any given time, thereby achieving effective mixing in the reactor over the entire period of deconstruction. Additionally, this sequential feeding of cellulose avoids having high concentrations of glucose in the reactor, thereby minimizing undesirable polymerization reactions (favored at high concentrations of glucose [16]) that lead to humins and which decrease the yield to levulinic acid. The levulinic acid yield is above 60% for the first cycle and gradually decreases with each cycle of cellulose addition, such that the final yield of levulinic acid is 52% after five cycles (Fig. 2a). A Ru/C catalyst is then employed at 423 K to convert the formic acid in the acid solution to CO<sub>2</sub> and H<sub>2</sub>, combined with the reduction of levulinic acid to GVL (Fig. 2b). Thus, the H<sub>2</sub> released by the decomposition of formic acid is utilized in the catalytic reduction of levulinic acid. Even though Ru catalysts have been reported to be ineffective in the presence of sulfuric acid [17,18], we note that use of appropriate concentrations of acid in the cellulose deconstruction reactor and subsequently in the hydrogenation reactor

**Table 1**

Ethyl acetate extraction of GVL in the presence of sulfuric acid.

GVL concentration	5 wt%	20 wt%				35 wt%		50 wt%	
H <sub>2</sub> SO <sub>4</sub> concentration	0.2 M	No acid	0.2 M	0.5 M	1.0 M	0.5 M	1.0 M	0.5 M	1.0 M
GVL extraction (%) <sup>a</sup>	73	75	76	75	76	82	82	87	86
H <sub>2</sub> SO <sub>4</sub> extraction (%) <sup>a</sup>	2	–	3	4	3	2	3	12	15
Water extraction (%) <sup>a</sup>	5	5	6	4	8	12	13	18	17

<sup>a</sup> % Extraction calculated as moles of compound transferred to the ethyl acetate layer divided by the moles of compound initially in the aqueous layer prior to ethyl acetate addition.

(0.5 M) allowed the Ru/C catalyst to achieve the desired conversion of levulinic and formic acids to GVL with high yield (Fig. 2b).

Management of the sulfuric acid used in the cellulose depolymerization step has been remarked as an essential aspect of biomass processing [19]. In this respect, ethyl acetate can be used to extract GVL selectively from the aqueous solution of sulfuric acid. While ethyl acetate has been proposed in the literature as an effective solvent for extraction of GVL from aqueous solutions [20], we note that previous studies have not addressed the selective extraction of GVL in the presence of sulfuric acid. In particular, when equal masses of ethyl acetate and the aqueous solution are contacted at room temperature, approximately 76% of the GVL and only 3% of the sulfuric acid are extracted into the organic phase (Table 1). We note that this extraction step is carried out at room temperature because sulfuric acid catalyzes the hydrolysis of ethyl acetate to ethanol and acetic acid at higher temperatures (e.g., 423 K), resulting in a single aqueous phase. When the extraction is performed at room temperature, only residual levels of ethanol and acetic acid were observed. It was observed that the percent of GVL extracted into the ethyl acetate layer increases with increasing GVL loading. The amount of water extracted into the ethyl acetate layer increased with increasing GVL extraction, while the sulfuric acid extraction increased only for the highest GVL concentration studied. Additionally, the effect of sulfuric acid concentration on the extraction of GVL and water was minimal for a 20 wt% GVL solution. The organic stream from the separator containing GVL can then undergo further catalytic processing following removal of the

ethyl acetate solvent in an evaporator. The concentrated GVL, containing residual levels of sulfuric acid and water is recombined with water to suitable levels (e.g., 30–40 wt% GVL) to help prevent coke formation in subsequent catalytic processing steps.

In recent work, we found that concentrated aqueous solutions of GVL can be catalytically processed, by means of ring-opening and hydrogenation reactions, over a bifunctional Pd(0.1%)/Nb<sub>2</sub>O<sub>5</sub> to produce an organic stream rich in pentanoic acid [11]. Nb<sub>2</sub>O<sub>5</sub> was chosen as a support because it provides good hydrothermal stability as well as sufficiently strong acidity to carry out GVL ring-opening under water environments. However, the GVL stream obtained after ethyl acetate extraction above described contains small amounts of sulfuric acid, thus requiring the development of sulfur-tolerant catalysts for the subsequent cascade processes depicted in Fig. 1. In this respect, Pd-supported materials have been reported to demonstrate sulfur resistance properties [21,22], and we found that by increasing the metal content to the level of 5 wt%, we could efficiently process synthetic aqueous streams of GVL (30–40 wt%) containing small amounts of sulfuric acid (0.02–0.04 M) at 548 K over a similar Pd/Nb<sub>2</sub>O<sub>5</sub> catalyst (Table 2). We note that these ranges of acid concentrations are typical of those obtained after the extraction strategy proposed herein to remove H<sub>2</sub>SO<sub>4</sub> from the solution produced by cellulose deconstruction. Over this Pd(5%)/Nb<sub>2</sub>O<sub>5</sub> catalyst, GVL was selectively converted to pentanoic acid for all ranges of acid and feed concentrations of the present study, and importantly, this pentanoic acid was stored in an organic layer that spontaneously separates from water and

**Table 2**

Processing of synthetic aqueous solutions of GVL and sulfuric acid.

Run	Catalyst	Feed (wt% GVL–M H <sub>2</sub> SO <sub>4</sub> )	T (K)/P (bar)/WHSV (h <sup>−1</sup> ) <sup>c</sup>	GVL conversion (%)	C distribution (%) <sup>a</sup>			C selectivity (%) <sup>b</sup>					
					Aq	Org	Gas	PA	C <sub>9</sub> =O	CO <sub>x</sub>	C <sub>4</sub> , C <sub>5</sub>	C <sub>5</sub> AL, C <sub>5</sub> OL	C <sub>6</sub> –C <sub>7</sub> Ket.
1	Pd/Nb <sub>2</sub> O <sub>5</sub>	30–0.02	548/14/0.5	100	–	87	13	78(1) <sup>†</sup>	–	2	16	3	–
2	Pd/Nb <sub>2</sub> O <sub>5</sub>	30–0.03	548/14/0.5	98	–	94	6	87(1) <sup>†</sup>	–	1	9	2	–
3	Pd/Nb <sub>2</sub> O <sub>5</sub>	30–0.04	548/14/0.5	94	1	94	5	89(–) <sup>†</sup>	–	1	8	2	–
4	Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.04	548/14/0.3	99	–	94	6	88(1) <sup>†</sup>	–	1	8	2	–
5	Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.03	548/14/0.3	98	–	95	5	88(1) <sup>†</sup>	–	1	7	3	–
6	Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.02	548/14/0.3	98	–	95	5	88(1) <sup>†</sup>	–	1	7	3	–
7	Pd/Nb <sub>2</sub> O <sub>5</sub>	30–0.02	538/14/0.5	97	–	94	6	86(1) <sup>†</sup>	–	1	9	3	–
8	Pd/Nb <sub>2</sub> O <sub>5</sub>	30–0.02	538/14/0.4	99	–	93	7	85(1) <sup>†</sup>	–	1	10	3	–
9	Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.04	548/14/0.7	84	1	97	2	92(–) <sup>†</sup>	–	1	5	2	–
10	Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.02	598/1/0.3	99	–	91	9	85(–) <sup>†</sup>	4(5) <sup>††</sup>	2	7	2	–
11	Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.02	548/14/0.8	100	–	89	11	–	80(89) <sup>††</sup>	9	4	–	7
12	Ce–Zr Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.02	698/14/0.5 548/14/0.8	98	–	95	5	73(–) <sup>†</sup>	18(19) <sup>††</sup>	2	5	1	1
13	Ce–Zr Pd/Nb <sub>2</sub> O <sub>5</sub>	40–0.02	623/14/0.5 548/14/0.8	98	1	92	7	47(–) <sup>†</sup>	40(45) <sup>††</sup>	5	5	2	1

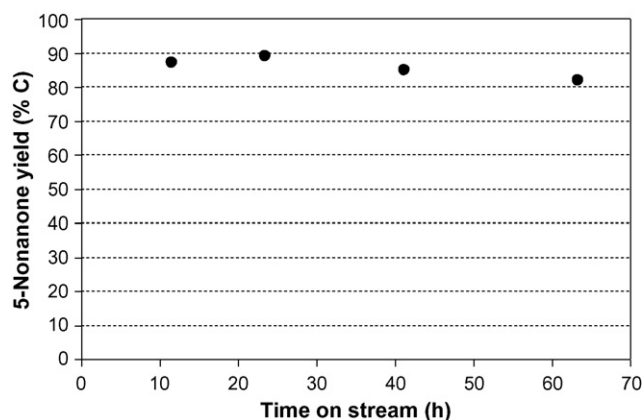
Values in parenthesis with † indicate C selectivity to the ester 1-pentyl pentanoate. Values in parenthesis with †† indicate C selectivity for 5-nonanone plus stoichiometric amounts of CO<sub>2</sub>.

<sup>a</sup> C distribution % for a phase i is calculated as (moles of carbon detected in phase i divided by the sum of moles of carbon detected in the three phases) × 100.

<sup>b</sup> C selectivity % for a product i is expressed as (moles of carbon as product i divided by the sum of moles of carbon for all the detected products) × 100.

<sup>c</sup> WHSV is defined by grams of GVL per hour fed to the reactor divided by grams of catalyst. PA: pentanoic acid; C<sub>9</sub>=O: 5-nonanone; CO<sub>x</sub>: CO and CO<sub>2</sub>; C<sub>4</sub>: n-butane; C<sub>5</sub>: n-pentane; C<sub>5</sub>AL: pentanal; C<sub>5</sub>OL: 1-pentanol; C<sub>6</sub>–C<sub>7</sub> Ket.: 2-hexanone and 3-heptanone.





**Fig. 3.** 5-Nonanone carbon yield versus time-on-stream for the Pd(5%)/Nb<sub>2</sub>O<sub>5</sub> + ceria-zirconia double-bed arrangement at 598–698 K, 14 bar, WHSV = 0.8–0.5 h<sup>-1</sup>, feed: 40 wt% GVL in water 0.02 M H<sub>2</sub>SO<sub>4</sub>.

accounted for approximately 95% of the carbon fed to the reactor (Table 2, runs 1–6). This organic phase also contained minor amounts of butane, pentane and pentanal/1-pentanol along with traces of 1-pentyl pentanoate and unreacted GVL. No carbon was present in the aqueous phase after the processing over Pd/Nb<sub>2</sub>O<sub>5</sub>, thus allowing the recycle of this water to the GVL stream. The carbon selectivity toward pentanoic acid was approximately 90% in all cases, except for the solution containing 30 wt% GVL–0.02 M H<sub>2</sub>SO<sub>4</sub> (Table 1, run 1) in which the selectivity (78%) and the amount of carbon stored in the organic layer (87%) decreased because of the formation of gaseous butane and pentane (16%). However, selectivities to pentanoic acid near 90% can be obtained for this specific feed by decreasing the reaction temperature (Table 2, run 7) and the space velocity (Table 2, run 8). An increase in the acid concentration from 0.02 to 0.04 M slightly decreased the conversion of the 30 wt% GVL solution (from 100% to 94%, Table 1, runs 1–3), while producing an increase in the selectivity to pentanoic acid (from 78% to 89%). In the case of the 40 wt% GVL feed, it was necessary to decrease the space velocity (only 84% conversion at a WSHV of 0.7 h<sup>-1</sup>, Table 2, run 9) by a factor of 2 to achieve nearly complete conversion of the reactant, with similar results for carbon distribution and carbon selectivities for all the acid concentration ranges (Table 2, runs 4–6).

A two-reactor configuration has been previously proposed to upgrade GVL to 5-nonanone [11]. Thus, the first reactor is loaded with Pd/Nb<sub>2</sub>O<sub>5</sub> and conditions are adjusted to maximize the yield to pentanoic acid in the organic stream, which is separated and serves as feed to the second reactor loaded with ceria-zirconia and operated at higher temperatures. In the present work, we show that 5-nonanone can be directly produced from aqueous acid solutions of GVL in a single reactor. For example, a 40 wt% GVL aqueous solution with a sulfuric acid concentration of 0.02 M (Table 2, run 11) can be efficiently converted to an organic stream (accounting for almost 90% of the carbon fed) enriched in 5-nonanone over a dual catalyst bed arrangement of Pd/Nb<sub>2</sub>O<sub>5</sub> followed by ceria-zirconia, with good stability versus time-on-stream (Fig. 3). 5-Nonanone is produced along with stoichiometric amounts of CO<sub>2</sub> and, if this CO<sub>2</sub> is included in the calculations, the C<sub>9</sub> ketone is generated with almost 90% selectivity (Table 2, run 11). The main by-products of the process were 2-hexanone and 3-heptanone, produced by scission of 5-nonanone in the alpha and beta positions, respectively. These by-products were also stored in the organic layer, and their presence would not affect the subsequent processes of the cascade approach depicted in Fig. 1 since they would form alkanes in the gasoline range (C<sub>5</sub>–C<sub>12</sub>). The residual sulfuric acid fed along with the GVL is completely converted to H<sub>2</sub>S after processing

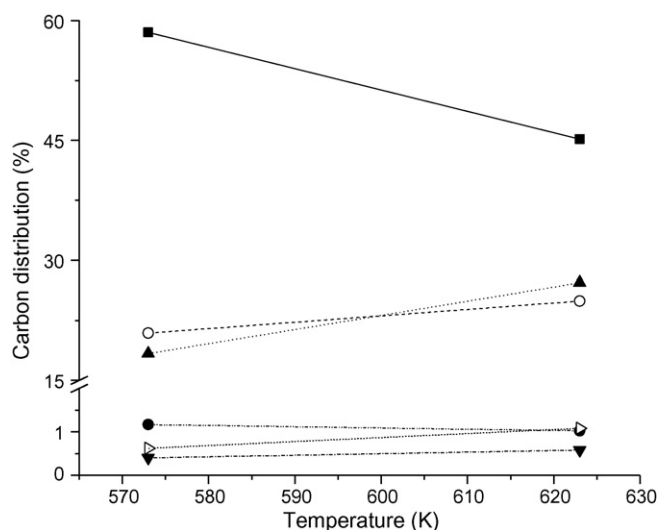
over Pd/Nb<sub>2</sub>O<sub>5</sub>. Therefore, no sulfur compounds were detected in the organic layer enriched in 5-nonanone. We note that the ceria-zirconia bed was operated at a higher temperature (698 K) than the Pd/Nb<sub>2</sub>O<sub>5</sub> bed (548 K) to achieve complete conversion of the pentanoic acid formed in the first catalyst bed (see Table 2, runs 12 and 13).

#### 4. Discussion

The cascade process for cellulose conversion described above has several advantages. For example, the progressive cellulose deconstruction described above is effective because we have shown that the levulinic acid and formic acid products are stable, and inert at our reaction conditions for cellulose deconstruction, allowing the accumulation of high levels of levulinic acid (e.g., 20 wt%) in the reactor after the deconstruction cycles. Additionally, the conversion of levulinic and formic acids to GVL in the presence of sulfuric acid eliminates the need of costly neutralization steps employed previously for this reaction [23]. Following the extraction of GVL with ethyl acetate, the aqueous solution containing sulfuric acid (and small amounts of GVL) can be recycled back to the cellulose deconstruction reactor, since the GVL in this recycled stream is inert during subsequent cellulose deconstruction. In addition to the favorable partitioning of GVL into ethyl acetate, this solvent is an excellent option for selective GVL extraction in view of the low vaporization heat of ethyl acetate (14% of the heat required to vaporize an equal mass of water), the possibility of generating it from renewable ethanol [24], and its benign health, safety and life-cycle properties [25].

Following the conversion of cellulose into the monofunctional 5-nonanone, there are several catalytic upgrading approaches that can be applied to produce diesel and jet fuel components. This C<sub>9</sub> ketone can be completely reduced to n-nonane by means of hydrogenation/dehydration cycles over a bifunctional metal-acid catalyst such as Pt/Nb<sub>2</sub>O<sub>5</sub> [26]. This nonane product possesses an excellent cetane number (72), heating value (45 kJ/g) and viscosity (0.96 mm<sup>2</sup>/s) for use in high-speed diesel engines. Additionally, the low melting point of nonane (220 K) makes this compound a good seasonal blending agent to improve flow properties and decrease the cloud point of current diesel fuels during cold weather. Moreover, the functional group of 5-nonanone can be used to control the structure and molecular weight of hydrocarbon fuel components formed in downstream catalytic upgrading treatment. For example, we have shown that 5-nonanol (the hydrogenation product of 5-nonanone) can be dehydrated and isomerized in a single step over an USY zeolite catalyst to produce a mixture of branched C<sub>9</sub> alkenes (Fig. 4) which can be optionally hydrogenated to produce alkanes with appropriate structures and molecular weight for use in gasoline applications. We note that the biomass derived 5-nonanone can also be converted into a C<sub>9</sub> alkene stream (by means of hydrogenation and dehydration reactions) which can be oligomerized over an acid catalyst to achieve good yields of C<sub>18</sub>–C<sub>27</sub> olefins, in the molecular weight range suitable for jet and diesel fuel applications [27].

Finally we note that the cascade approach described herein to convert cellulose can be integrated with existing processes to convert the hemi-cellulose and lignin fractions of lignocellulosic biomass. For example, hemi-cellulose can undergo hydrolysis to produce xylose [28], which can be used to produce H<sub>2</sub> and CO<sub>2</sub> by aqueous-phase reforming [29], or to produce furfural [30]. The lignin fraction of biomass and solid humins (formed during the cellulose processing to GVL) can undergo gasification [31] to produce H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub>. Importantly, the catalytic upgrading of GVL to pentanoic acid herein described can be carried out at atmospheric pressure (see Table 2, run 10), allowing the potential use of H<sub>2</sub>-



**Fig. 4.** Carbon distribution for the dehydration and isomerization of 5-nonanol over USY zeolite at atmospheric pressure and a WHSV of  $0.6\text{ h}^{-1}$  at various reaction temperatures to n-nonene (■), C<sub>1</sub>-octene<sup>a</sup> (○), C<sub>2</sub>-heptene<sup>a</sup> (▲), C<sub>3</sub>-hexene<sup>a</sup> (▼), cracking products<sup>b</sup> (●) and aromatics<sup>c</sup> (▷). (a) C<sub>1</sub>–C<sub>3</sub> refers to hydrocarbon branches: C<sub>1</sub>: methyl, C<sub>2</sub>: ethyl, dimethyl, C<sub>3</sub>: propyl, ethyl/methyl, trimethyl; (b) alkenes with less than 9 carbon atoms; (c) trimethyl benzene, ethyl/methyl benzene.

enriched streams from biomass gasifiers for the GVL reduction to pentanoic acid, without the need of costly compression steps. In addition, pyrolysis could be employed to convert lignin and solid humins to bio-oils [32] or to aromatic fuels [8].

## 5. Conclusions

Cellulose can be converted to liquid hydrocarbon fuels (with structure and molecular weight appropriate for gasoline and diesel applications) using a cascade approach that achieves progressive deoxygenation of the biomass derivatives. This approach allows a better control of reactivity and facilitates separation of products generating spontaneously separated from water streams with high yields. Cellulose is initially hydrolyzed (in diluted sulfuric acid solution) to glucose which is dehydrated to generate a mixture of formic acid and levulinic acid. This mixture can be transformed into GVL without the need of neutralization steps over a Ru/C catalyst. The formation of GVL is an important step because it allows: (a) effective extraction strategies with ethyl acetate for the management and recycling of the H<sub>2</sub>SO<sub>4</sub> used in the depolymerization step; and (b) subsequent catalytic upgrading approaches to produce, in a single reactor, organic streams enriched in 5-nonanone, a precursor to hydrocarbon fuels.

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